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RELATED PCT APPLICATION NUMBER: *PCT/US04/19188*

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PTO/SB/16 (10-01)
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

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☑ Additional inventors are being named on the 1 separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

Sidewall functionalization of nanotubes with hydroxyl terminated moieties

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ENCLOSED APPLICATION PARTS (check all that apply)

☑ Specification Number of Pages 6

☐ Drawing(s) Number of Sheets

☐ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number

☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☑ A check or money order is enclosed to cover the filing fees

☑ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 23-2426

☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE AMOUNT ($) $80.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE _____ Date 07/28/2003

TYPED or PRINTED NAME Robert C. Shaddox REGISTRATION NO. (if appropriate) 34,011

TELEPHONE (713) 650-2764 Docket Number: 11321-P073V1

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (02-01)
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Docket Number	11321-P073V1

INVENTOR(S)/APPLICANT(S)

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Number 2 of 2

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Sidewall functionalization of nanotubes with hydroxyl terminated moieties

Description of the invention:

Two new chemical methods for preparation of previously unknown "hydroxyl-nanotubes" have been developed

Technical description

Two simple and inexpensive methods for preparation of nanotubes sidewall functionalized with organic groups terminated with hydroxyl moieties have been developed. Both methods use fluoronanotubes as precursors. In the first method they react with diols and triols, pre-treated with LiOH. In the second method, the reactions with amino alcohols in the presence of pyridine are applied. The series of "hydroxyl-nanotubes" prepared by these methods show improved solubility in ethanol, isopropanol,chloroform, and other polar solvents, which is important for application processing in the fabrication of nanotube-integrated polymer composites and ceramics as well as for compatibility with bio-systems.

The developed methods for preparation of "hydroxyl-nanotubes"are simple, efficient, and ready for scale-up. Potential uses of "hydroxyl-nanotubes"are in polymer composites and ceramics, bio-systems, and as a synthons for further derivatization.

No similar methods for this type of sidewall functionalizations exist.

Variations

Possible modifications may invilove attachment of the thiol (-SH) terminated functionalities to the sidewalls of nanotubes and extension of demonstrated methods to multi-walled and double-walled nanotubes.

Detailed technical description:

Sidewall functionalization of nanotubes with hydroxyl terminated moieties

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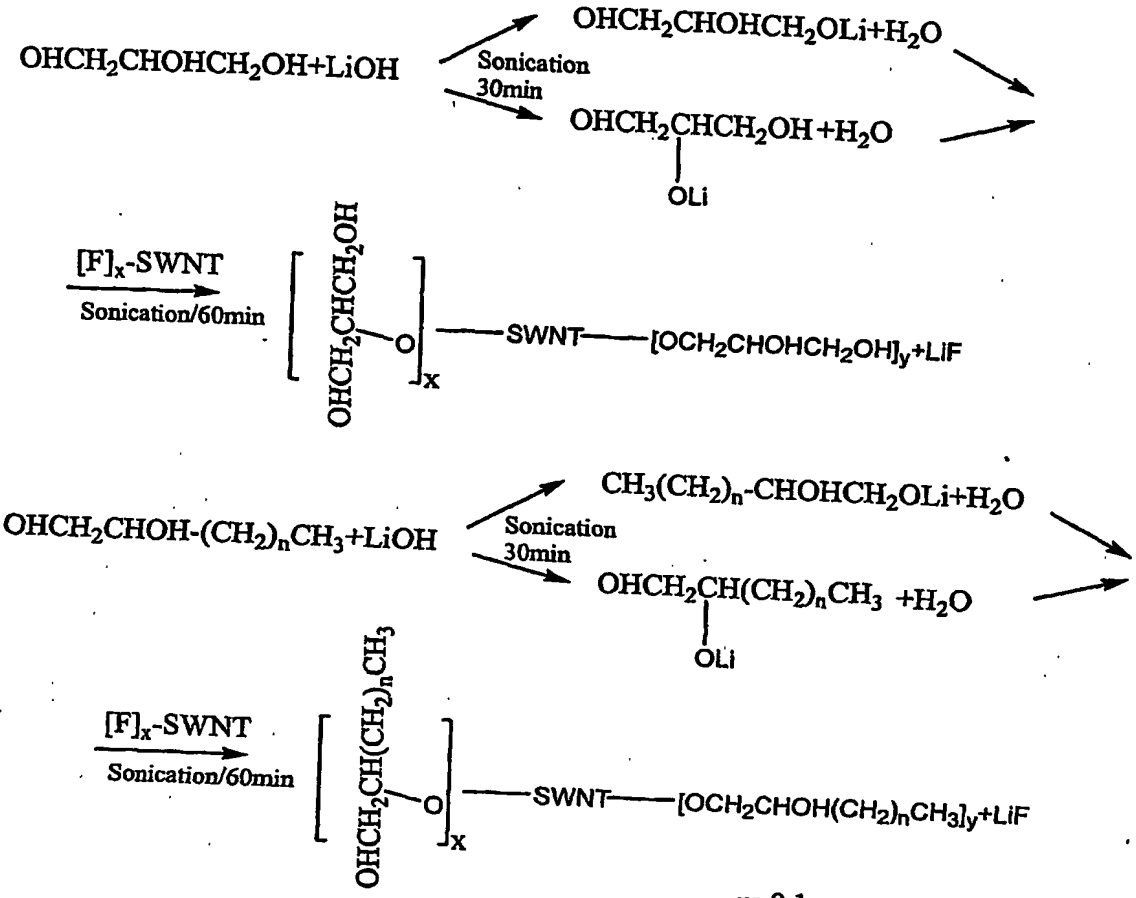
For applications in design of functional nanotube-based materials, the nanotubes need to be functionalized to bear organic groups, which show a high binding affinity and selectivity through either hydrogen bonds or chemical interactions to form new covalent linkages. For medical and biological application the nanotubes must be chemically derivatized with hydrophilic substituents, such as those containing hydroxyl or carboxylic acid groups. These functional groups are also necessary for providing sites for covalent integration into organic/inorganic polymer composite structural materials and ceramics. In the present work, we will present two developed methods for preparation of nanotubes sidewall functionalized with organic groups containing terminal hydroxyl moieties.

By following the first method, we reacted a series of diols and triols, pre-preated with LiOH, with the fluoronanotubes (see scheme).

$$OH(CH_2)_nOH+LiOH \xrightarrow[30min]{Sonication} OH(CH_2)_nOLi+H_2O$$

$$OH(CH_2)_nOLi+[F]_x\text{-SWNT} \xrightarrow[60min]{Sonication} [OH(CH_2)_nO]_x\text{-SWNT}+LiF$$

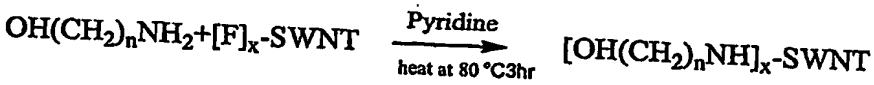
$$n=2,3,4$$



n=0,1

We have studied ethylene glycol, 1,3-propanediol, 1,4- butanediol, 1,2-propanediol, 1,2-butanediol and glycerol in these experiments.

The second method is based on the reaction of amino alcohols with the fluoronanotubes in the presence of pyridine as the catalyst (see scheme).



n=2,3

Amino ethanol and 3-amino 1-propanol have been studied in this reaction.

The following typical experimental procedures have been developed for the functionalization:

First Method: Fluoronanotubes (10-15mg) were sonicated in 10ml of diol or triol for 30 min in order to achieve complete dispersion of the fluoronanotubes. LiOH (60-80mg) was sonicated separately in 10ml of the same diol or triol for 30 min in order to dissolve completely and produce enough hydroxyl terminated RO^- groups. After sonication, the dispersions were joined together and the mixture sonicated for 1 hr. Then the reaction mixture was filtered through a 1-micron pore size Cole Palmer Teflon membrane, washed with a large amount of ethanol and water to assure complete removal of LiOH, LiF, and reaction byproducts. Finally, the resulting blacked-colored films were peeled off the membrane and dried overnight in vacuum oven at 70 °C. The prepared samples have been characterized by ATR-FTIR, Raman and TGA analysis. According to the TGA, the degree of sidewall functionalization achieved for the hydroxyl nanotubes was 1 in approximately 8 carbons.

Second Method: Fluoronanotubes (10-15mg) were sonicated in 30ml amino alcohol for 3 min. Then five drops of pyridine were added to the obtained solution. The reaction mixture was stirred at 80-90 °C under nitrogen purge for 3hr. Then the reaction mixture was filtered through a 1-micron pore size Cole Palmer Teflon membrane with a large amount of ethanol to assure complete removal of unreacted amino alcohol, LiF and reaction byproducts. Finally, the resulting blacked-colored films were peeled off the membrane and dried overnight in vacuum oven at 70 °C. The prepared samples have been characterized by ATR-FTIR, Raman and TGA analysis.

The "hydroxyl-nanotubes" prepared using these methods show improved solubility in ethanol, chloroform, and other polar solvents.

Grant or Contract Number:

Welch Foundation of Texas Grant C-0109; Texas Higher Education Coordinating Board, ATP Grant 003604-0026-2001.

Claims

What is claimed:

1. A method comprising:
   a) reacting a species, $HO(CH_2)_nOH$, with LiOH to yield $HO(CH_2)_nOLi$; and
   b) reacting $HO(CH_2)_nOLi$ with fluorinated single-wall carbon nanotubes, $[F]_x$-SWNT, to yield single-wall carbon nanotubes functionalized with hydroxyl terminated moieties, $[HO(CH_2)_nO]_x$-SWNT.
2. The method of Claim 1, wherein $n = 2,3,4$, or combinations thereof.
3. The method of Claims 1 or 2, wherein the degree of sidewall functionalization is about one functional group per every eight nanotube carbons.
4. The method of Claims 1-2, or 3, further comprising a purification step wherein the product is washed with an alcohol to remove unwanted reaction by-products.
5. The method of Claims 1-3, or 4, wherein the single-wall carbon nanotubes functionalized with hydroxyl terminated moieties, $[HO(CH_2)_nO]_x$-SWNT, show improved solubility in polar solvents relative to unfunctionalized single-wall carbon nanotubes.
6. A method comprising:
   a) selecting a plurality of fluorinated single-wall carbon nanotubes, $[F]_x$-SWNT; and
   b) reacting said fluorinated single-wall carbon nanotubes with an amino alcohol, $HO(CH_2)_nNH_2$, in the presence of pyridine to yield $[HO(CH_2)_nNH]_x$-SWNT.
7. The method of Claim 6, wherein $n = 2,3$, or combinations thereof.
8. The method of Claims 6 or 7, further comprising a purification step wherein the product is washed with an alcohol to remove unwanted reaction by-products.
9. The method of Claims 6-7, or 8, wherein the product is dried in vacuum at an elevated temperature.

10. The method of Claims 6-8 or 9, wherein the single-wall carbon nanotubes functionalized with hydroxyl terminated moieties, $[HO(CH_2)_nNH]_x$-SWNT, show improved solubility in polar solvents relative to unfunctionalized single-wall carbon nanotubes.

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